

## TRANSLATION

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(71) Applicant : 000003207  
Toyota Automobile Co.  
1, Toyota-cho, Toyota-shi, Aichi-ken

(72) Inventor : Toshihiro Takada  
Toyota Automobile Co. 1, Toyota-cho, Toyota-shi, Aichi-ken

(74) Agent : Patent Attorney, Hiroshi Okawa

### (54) [Title of the Invention]

#### Method to Produce the Exhaust Gas Cleaning Catalytic Converter

### 57. [Summary]

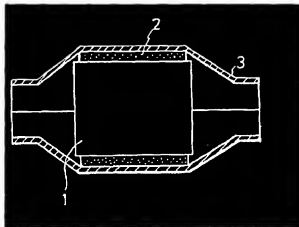
#### [Objective]

A ceramic seal and a metal support are strongly fixed without using an adhesive agent, etc.

#### [Structure]

Production method in which an activated alumina layer is formed on the metal support made out of an aluminum- containing alloy, except for the outer most circumference surface, to make it into the catalyst, and the outer most circumference surface of the metal catalyst support 1 is covered with the ceramic sealing material 2, and thereafter, the metal catalyst support is heated and the alumina whiskers are grown on the outer

most circumference surface, and by bonding the ceramic seal material and the alumina whiskers as one body, the ceramic sealing material 2 and the metal catalyst support 1 are fixed as one body.



- 1; Metal catalyst support
- 2; Ceramic seal material
- 3; Container

#### **[Scope of the Patent Application]**

##### **[Claim 1]**

Method to produce the catalytic converter for cleaning the exhaust gas characterized by the fact that it is comprised of the first stage in which an activated alumina layer is formed on the metal support which is honey comb shaped and made out of an aluminum- containing alloy, except for the outer most circumference surface, to make it into the catalyst, and the second stage in which the outer most circumference surface of the said metal support that was made into the catalyst is covered with a ceramic sealing material in a cylindrical shape, and it is stored in the container, and that the said second stage includes the stage which heats the said metal support that was covered with the said ceramic sealing material and in which alumina whiskers are grown on the outer most circumference surface of the said metal support and the said ceramic seal

material and the said alumina whiskers are bonded as one body.

**[Detailed Explanation of the Invention]**

**[0001]**

**[Field of Utilization in Industry]**

This invention relates to the method to produce the exhaust gas cleaning catalytic converter in which the metal support is stored. According to the method of this invention, the relative shifting of the container and metal support can be surely prevented.

**[0002]**

**[Existing Technology]**

Concerning the exhaust gas cleaning catalytic converter which cleans the exhaust gas from the car engine, etc., the one in which the metal catalyst is supported by the metal support, and that is stored in the container, has been known. Concerning the method to produce this type of catalytic converter, the foil like flat sheet and wave shaped sheet formed from the ferritic alloys that includes aluminum, are wound, and the metal support is formed. Then, the catalyst support layer made out of activated alumina, is formed on the surface of this metal support, and the catalyst metal is supported by this catalyst support layer, and then it is made into the catalyst. This metal support which was made into the catalyst, is stored in a container, and this is the catalytic converter. The support for this metal honey comb catalyst is made out of a foil like metal, therefore, its heat conductivity is high and also its heat capacity is small, compared with the monolith type support, etc., so that the temperature rises quickly, and it has excellent cleaning performance at the time of initiation.

**[0003]**

By the way, since the the metal support is so thin, various measures have been used

for the fixing method. For example, it can be inserted into an outer cylinder made out of metal with about a 1.5 mm thick wall, and then it is connected and fixed by brazing. However, with this method, the thermal stress is generated due to the difference in thermal expansion coefficients between the metal support and the outer cylinder, and sometimes, the metal support is broken. Therefore, the brazing position, etc., must be carried out with this in mind. In addition, the heat of the metal support is conducted easily to the outer cylinder, and this heat conduction causes heat loss, and also the sound that is radiated due to the exhaust pulsation tends to become larger too.

**[0004]**

Therefore, in some methods, both ends of the metal support are fixed by retainers. Or, there is the method in which the metal support is covered with a sealing material such as ceramic wool, etc., and this covered material is stored in the container and it is fixed, as the fixation method for the ceramic honey comb body, as was disclosed in Patent Kokai No. H2-43955 Official Gazette, and Patent Kokai No. H2-86847 official Gazette, etc.

**[0005]**

**[Problem That this Invention Intends to Solve]**

In the method of fixing both ends of the metal support by a retainer, the stress generated in the metal support by thermal expansion can not be absorbed, and the heat loss also occurs through the retainer. On the other hand, if the sealing material such as ceramic wool, etc., is used, it will have a good effect for improving the hot gas retention and for decreasing the radiated sound due to its heat insulating effect and the sound absorbing effect. In addition, it also has appropriate elasticity, therefore, the stress due to the thermal expansion of the metal support can be absorbed, and the breakage of the metal support can be prevented too.

**[0006]**

However, in the fixation method that uses sealing material, the strength of the metal support itself is low, so that it can not be tightened strongly, and the fixing strength between the sealing material and the metal support is naturally small, so that the metal support moves in the axial direction or in the circular direction relatively to the sealing material, by the vibration, etc., during the time when it is being used, and this is not good. The above mentioned Patent Kokai No. H2-43955 disclosed that the ceramic honey comb support surface that contacts with the sealing material is made to be a roughened thermal sprayed surface, and the sealing material bonds into the thermal sprayed surface, so that the ceramic honey comb support and the sealing material are strongly fixed. Patent Kokai No. H2-86847 disclosed that the surface of the ceramic honey comb support can be roughened by sand blast treatment, etc., to improve the fixation strength. However, the thickness of the flat sheet and the waved sheet of the metal support is extremely small, therefore, it is difficult to apply the method described in the above mentioned official gazette "as is" for bonding the metal support and the sealing material.

**[0007]**

This invention was made considering the situation like this, and its objective is to strongly fix the sealing material and the metal support.

**[0008]**

**[Method to Solve the Problem]**

In order to solve the above mentioned problems, the method to produce the exhaust gas cleaning catalytic converter of this invention is characterized by the fact that it is comprised of a first stage in which an activated alumina layer is formed on the metal support which is honey comb shaped and made out of an aluminum- containing alloy, except for the outer most circumference surface, to make it become the catalyst, and a

second stage in which the outer most circumference surface of the metal support that was made into the catalyst is covered with a ceramic sealing material of a cylindrical shape, and it is stored in the container, and that this second stage includes the stage which heats the metal support that was covered with the ceramic sealing material and in which alumina whiskers are grown on the outer most circumference surface of the metal support and the ceramic seal material and alumina whiskers are bonded as one body.

**[0009]**

There are following methods to form the activated alumina layer on the metal support except for the outer most circumference surface in the first stage:

the method in which the activated alumina layer is formed on the entire metal support, and thereafter, the activated alumina layer on the outer most circumference surface is removed by grinding, etc., or

the method in which the activated alumina layer is formed under the conditions in which the outer most circumference surface was protected by masking, etc.

In this way, the aluminum- containing alloy is exposed on the outer most circumference surface of the metal support. Here, the same as before, the noble metal catalyst metal such as platinum, rhodium, etc., or the non-noble metal catalyst metal are supported on the activated alumina layer, and it is made into the catalyst.

**[0010]**

In the second stage, after the metal support is covered with the ceramic seal material, or after the metal support covered with the ceramic seal material is stored in the container and made to be a catalytic converter, the metal support is heated. This heating can be done intentionally in a heating process, or it can be done by being

heated by the exhaust gas during the time when it is used as the exhaust gas cleaning catalyst. Due to this heating, the alumina whiskers are formed on the surface where the aluminum- containing alloy is exposed on the metal support, and these whiskers grow while incorporating the ceramic fibers of the ceramic seal material, therefore, the metal support and the ceramic seal material are connected into one body. Therefore, the ceramic seal material should be preferably the one which has high miscibility with alumina whiskers, and the ones which contain alumina are preferred. For example, the sealing material comprised of non- expanded vermiculite, inorganic fibers, organic elastic binder, etc. ("Ibiwool?" (*spelling uncertain, Translator*) a product of Ibiiden? (*spelling uncertain, Translator*) K.K.), or the insulation material made out of ceramic fibers such as alumina, silica, etc. ("Kaowool 1400" a product of Isolight? (*spelling uncertain, Translator*) Industry K.K.), can be listed.

**[0011]**

**[Action]**

In the production method of this invention, the ceramic seal material is put on the metal support in which an aluminum- containing alloy is exposed on the outer most circumference surface, and it is heated in this condition. Then, the surface of the exposed aluminum- containing alloy is oxidized, and alumina whiskers will grow. Alumina whiskers grow while incorporating the ceramic seal material, and also the anchoring effect can be obtained since the alumina whiskers bond into the seal material, therefore, the metal support and the ceramic seal material are bonded strongly as one body.

**[0012]**

**[Actual Examl ]**

Next, this invention will be explained concretely referring to actual examples.

**(Example 1)**

**[ First Stage]**

A flat sheet and a wavy sheet were made by using 50  $\mu\text{m}$  thick foil made out of an aluminum- containing ferritic alloy (Fe - 20Cr -5Al), and these were placed one upon another, and wound into a roll, and the metal support with 100 mm diameter and 100 mm long was made. Next, this metal support was submerged in a slurry consisting of activated alumina, water and binder. Then, the metal support was pulled out from the slurry and the excess slurry was blown off, and it was dried at 100 °C for 1 hour, then it was baked at 700 °C for 2 hours. Thus, the catalyst support layer which consists of activated alumina all over the surface of the metal support, was formed.

**[0013]**

Then, the whole assembly was submerged in an aqueous solution of di-nitro di ammine palatinum for 1 hour. It was taken out of the solution and excess solution was blown off, and thereafter, it was dried at 120 °C for 2 hours, and thus the platinum was supported at a concentration of 1 g of platinum per 1 L of support. Next, it was submerged in an aqueous solution of rhodium chloride, and the rhodium was supported in the same way at 0.2 g per 1 L of support, and thus, the supported metal catalyst was obtained.

**[Second stage]**

The outer most circumference surface of the above mentioned supported metal catalyst was ground by sand paper, and the catalyst support layer that includes the noble metal catalyst was removed and the alloy surface was exposed. Although sand paper was used here, it can be ground by using shot blasting, buff abrasive work, etc., too.

**[0014]**



Next, the ceramic seal material 2 which was comprised of 69.2 wt % of un-expanded vermiculite treated with an organic amine, 26.0 wt % of alumina type ceramic fibers ("Ibiwool?" made by Ividen? Co.), 2.8 wt % of acrylonitrile butadiene and 2.0 wt % of montmorillonite, was prepared, and as can be seen in Figure 2, it was wrapped around the metal catalyst support 1 that was ground as described above, and then, it was stored in the clam shell type container 3 which can be split in two as can be seen in Figure 1, and the container 3 was welded under increased pressure, and this is the catalytic converter of this invention.

#### [0015]

This catalytic converter was installed in the exhaust system of an inline 6 cylinder, 3000 cc gasoline engine, and an endurance test in which the 2 types of driving conditions indicated in the Table were repeated for 600 cycles, was performed.

#### [0016]

**[Table 1]**

Air fuel ratio (A / F)	Rotation (rpm)	Engine negative pressure (mm Hg)	Entering gas temperature	Time
14.5	3000	- 360	850 °C	10 min
14.5	700	- 360	450 °C	10 min

During the endurance test, the catalytic converter was taken off every 100 cycles, and the shifting of the metal catalyst support 1 was visually checked. The results are shown in Table 2. In this actual example, it was confirmed that the ceramic seal material 2 and the metal catalyst support 1 were tightly attached after 600 cycles. This is due to the fact that the alumina whiskers grew on the surface of the metal support, and it bonded with the ceramic seal material that contains alumina fibers.

#### (Comparison 1)

A catalytic converter was produced the same as in Example 1, except that the surface of the metal support was not ground in the second stage, and the endurance test was performed in the same way. The results are shown in Table 2.

### (Comparison 2)

In the first stage of Example 1, protrusions were formed on the outer most circumference surface of the metal support that has the catalyst support layer, and thereafter, the noble metal catalyst was supported in the same way. Then, the second stage was done the same as in Example 1, and the catalytic converter was produced, and the endurance test was performed in the same way. The results are shown in Table 2. Here, the protrusions were such that the diameter was 2 mm, and height was 1 mm, and these were provided at 5 mm intervals from the centers of the protrusions in a lattice format over the entire surface of the outer most circumference.

### (Evaluation)

[0017]

**Table 2]**

	Result	Evaluation
Example 1	No change after 600 cycles	O
Comparison 1	Metal support moved backward from the seal material after 100 cycles	X
Comparison 2	Metal support moved backward from the seal material after 300 cycles	X

According to the method of Example 1, the outer most circumference surface of the metal support that was ground becomes oxidized since it is heated by the heat of the exhaust gas during the time of conducting the endurance test, namely when it is being used, and the alumina whiskers grow. These alumina whiskers grow while incorporating the fibers of the ceramic seal material, and thus the ceramic seal material

and the metal support are tightly bonded. Therefore, even if the thermal stress works during the endurance test, they are bound in one body and do not shift from each other.

**[0018]**

On the other hand, in the Comparison example in which the grinding was not done, a slight effect could be seen by providing the protrusions, however, the bonding strength that is similar to that in the Example could not be obtained, so it moved due to the thermal stress.

**[0019]**

**[Effect of the Invention]**

Therefore, according to the production method of this invention, the metal support and the ceramic seal material can be made as one body easily by simply heating the assembly. Therefore, there is almost no need to increase the processing steps, and it is advantageous cost wise. If it is heated by the exhaust gas heat during the time of usage, the number of process steps can be reduced even more. Further, since it can be stored in the split style container without using an outer cylinder and without brazing, the expensive brazing material or the high temperature high vacuum heat treatment become un-necessary, and it can be produced at even lower cost.

**[0020]**

In addition, by use of the catalytic converter obtained, the hot air can be increased and the sound radiation can be reduced, since it has a ceramic seal. Also, the parts are bound together by alumina whiskers, therefore, the inconveniences such as the ceramic seal material moving relative to the metal support during the time when it is being used, can be surely prevented.

**[Simple Explanation of Figures]**

**[Figure 1]**

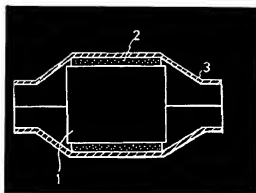
This is the cross section of the catalytic converter produced in an actual example of this invention.

**[Figure 2]**

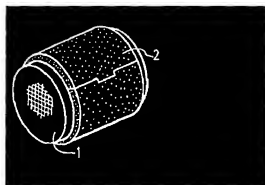
This is an angled view which indicates the state in which ceramic seal material was wrapped around the metal support in the actual example.

**[Explanation of Marks]**

- 1; Metal catalyst support
- 2; Ceramic seal material
- 3; Container



- 1; Metal catalyst support
- 2; Ceramic seal material
- 3; Container



1; Metal catalyst support

2; Ceramic seal material

*[The remainder of the pages was corrections, and these were corrected in the translation, Translator]*